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Oil/Water Interface (1)

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Surface Impurities Are Not Responsible For the Charge on the Oil/Water Interface: A Comment[**]

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A recent communication by Roger and Cabane[1] on the origin of negative charge on the interface between oil and water states that: "The basic assumption of all previous experimental and theoretical studies has been that these systems have "pristine" oil/water interfaces, that is, oil molecules in contact with water molecules, although the possibility of contamination by anionic, surface-active impurities has been mentioned." It is asserted that long-chain carboxylic acids could originate as impurities from the oil phase. These impurities might be responsible for the unusually large surface charge on the oil/water interface. Covering the interface with carboxylic ions would lead to a reduced interaction of oil with water. This claim is supported by a self-consistent data set[1] comprised of 1) droplet mobility data as a function of pH, 2) droplet size distribution measured for different grades of impurity and with different concentrations of carboxylic acid, and 3) a titration experiment to quantify the amount of acid in the hexadecane oil phase. While this data is of interest its weakness appears to be that none of the employed methods are in situ background-free measurements of interfacial chemical structure. The surface sensitivity of the employed methods relies on the application of crucial assumptions about the surface structure, mean field theories, and non-equilibrium methods.

Previously, we reported that the water orientation near the oil droplet interface as a function of pH[2] was found to be indistinguishable of a negatively charged surface, and unchanging as a function of pH. We made those statements based on results obtained from electrokinetic mobility measurements and vibrational sum frequency generation (SFG)[3] scattering (SFS)[4] experiments. For different pH values charge densities were reported in the range of -0.008–$0.42\,e\,\mathrm{nm}^{-2}$. SFS is a technique that is both interface specific and chemically sensitive. Here, we report that our observations on the nature of the oil/water interface are not due to surface impurities.

Vibrational SFG can be used to measure the coherent vibrational spectrum of the less than 1 nm thick shell that contains a droplet interface. The sum frequency signal is background free and originates from a combined Raman and IR process, which occurs for symmetry reasons only at interfaces of isotropic media. It is also an in situ technique and model independent, in contrast to, for example, mobility measurements or neutron scattering. Mobility measurements rely on the assumption that charges (ions) are the only source for mobility, which happens under slip-free conditions. In neutron scattering the density of (H) atoms is measured for an interface between isotopically contrast-balanced media, and the surface structure is derived from a fit with a form factor function that represents a certain molecular configuration.

SFG has been used in the past to measure structural changes on the air/water interface following changes in the bulk concentration as low as picomolar concentrations[3e]. It has also been used to investigate the planar oil/water interface. No surface impurities were reported in these studies.[3a-c] Since the surface-to-volume ratio for a planar interface is far smaller than that of a droplet system, an expected droplet surface density of $0.42\,\mathrm{charges\,nm}^{-2}$ would translate (with identical bulk concentration) to a much larger impurity density on the planar oil/water interface.

In an SFS experiment the interfacial layer is characterized by 1) the vibrational frequencies of the interfacial chemical units (i.e. water/oil/surfactant), 2) the coherent interference between similar frequency components of the corresponding chemical groups, and 3) the ratio of the polarization combinations PPP, SSP, and SPS. The spectral shape is mostly independent of the droplet size and scattering angle, up to a radius (R) of about 300 nm.[4] The polydispersity index (PDI) does not influence the spectral shape either. Surface presence or absence of a chemical bond can be confirmed by measuring the intensity at a certain frequency. Furthermore, selective deuteration can be used to shift vibrational modes in and out of the spectral region of interest so that apart from interference spectra, interfacial oil, water, and surfactants can be probed independently.

The water orientation near the oil droplet interface as a function of pH[2] was extracted from the interference of the blue spectral part of the O−D stretch motion of the deuterated water phase and the C−H stretch modes present

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in the oil. We have observed neither new frequency components, nor different spectral interference terms, nor an increase/decrease in the O–D vibrational intensity. A changing O–D (or O–H) intensity occurs under the influence of (surfactant) ions.[5]

The same oil/water spectra show that no changes occurred in the average carbohydrogen structure at the interface. If for example, there had been oleic acid at the interface we would have observed some change in the C–H stretching region, which would include a change in the interference pattern[5] as well as the appearance of new frequency components indicative of the double bonded =C–H stretch mode. Also, we would have seen a change in the dispersive spectral tail of the O–D stretch region (2750–2850 cm^{-1}), which is reminiscent of an increase in surfactant ions at the interface.[5a] With a detection limit better than one molecule per 27 nm^2 (for radii of about 100 nm), SFS would have shown us direct evidence of impurities in the amounts needed to originate from charge densities of up to $-0.42\ e\,nm^{-2}$.

The possibility of impurities is, however, a returning topic in emulsion science. Furthermore, it could be that carboxylic acid impurities are in some way invisible to our instrument. Since we have the ability to measure spectroscopically the surface species, we have performed additional experiments using deliberate carboxylic acid impurities. We have prepared emulsions as described in Ref. [2] using both 99 and 99.8% pure hexadecane, and we have taken hexadecanoic acid (HDA) as a deliberate impurity, which is as close as possible in chemical structure to the hexadecane oil molecule (and therefore presumably difficult to detect). Droplet samples were prepared with 1) 1 vol% of $C_{16}H_{34}$ droplets ($R = 100$ nm, PDI = 0.20) in D_2O under pH neutral conditions, 2) 1 vol% of $C_{16}H_{34}$ droplets ($R = 99$ nm, PDI = 0.21) in D_2O with pH 12, 3) 1 vol% of $C_{16}D_{34}$ droplets ($R = 83$ nm, PDI = 0.17) in D_2O under pH neutral conditions with hexadecanoic acid (HDA) in different concentrations, and 4) 1 vol% of $C_{16}H_{34}$ droplets ($R = 83$ nm, PDI = 0.18) in D_2O under pH neutral conditions with different concentrations of hexadecanoic acid. HDA concentrations of 50 μM to 5 mM were measured. Samples (1) and (2) are used as a reference to our previous published data. Sample (3) will show us the conformation of interfacial HDA ions since the C-D vibrational resonances of the oil do not appear in the probed spectral region. Since the amount present at the interface is directly detected, it should be noted that it is irrelevant which preparation procedure was used or to which bulk phase the HDA is added; it can be detected down to the detection limit of our instrument. Sample (4) would be representative of an impure sample if the impurity originated from the oil phase. If our result had been caused by surface impurities, we would expect samples (1) and (2) to be different, and samples (2) and (4) to be identical.

Figure 1 shows SFS spectra of samples (1) and (2) in Figure 1 A, and sample (3) in Figure 1 B. Figure 1 A shows that there is no change in the chemical surface structure at different pH values. We observe no additional interference, no new vibrational modes, and no change in the water structure that would be reminiscent of the presence of ions upon changing the pH value. Furthermore, spectra recorded with 99 and 99.8 % pure oil showed the same results. Based on Figure 1 alone, one could conclude that maybe there are acid contaminations at the interface, but they do no change their structure with pH (except from losing an H^+ ion). Also, one could argue that the ionization process might not be observed in the O–D stretch region for this particular acid. Figure 1 B shows the vibrational surface spectrum of sample (3) and removes these doubts: we see an increase in the dispersive tail of the O–D stretch mode (arrow). Furthermore, the CH_3 stretch modes stand out as dominating the spectrum. Especially in the SPS polarization ratio, the asymmetric CH_3 stretch mode (r^-) is the dominant peak. At much lower concentrations similar distinct spectral features of HDA are visible.

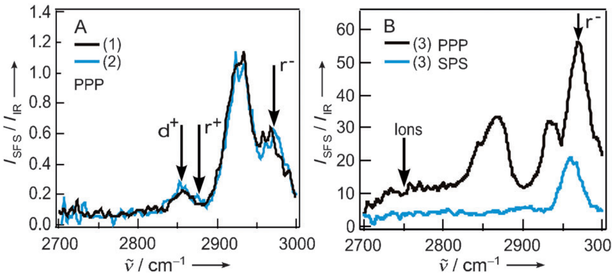

Figure 1. Vibrational sum frequency spectra showing the coherent interfacial vibrational spectrum of (A) the *n*-hexadecane droplet/D_2O interface at neutral pH and pH 12. The polarization combination used was PPP, and B) the $[D_{34}]$-*n*-hexadecane/D_2O droplet interface, with 5 mm hexadecanoic acid to the solution. The vibrational resonances of the symmetric methyl and methylene stretches (d^+, r^+) and the antisymmetric methyl stretch (r^-) mode are clearly visible. SSP data provided no new information. S-polarized light oscillates perpendicular to the plane of incidence and P-polarized light oscillates parallel to the plane of incidence, and the order of the beams is sum frequency (SF), visible (VIS), and infrared (IR).

Figure 2 shows a comparison of sample (2) and sample (4) using polarization combinations PPP (Figure 2 A) and SPS (Figure 2 B). We see that the spectrum of the deliberately contaminated sample (4) displays clear traces of the acid. The dominant modes in these spectra are the methyl stretch modes (r^+ and r^-). Especially the SPS spectrum of sample (4) shows a single large r^- peak. These spectral differences are

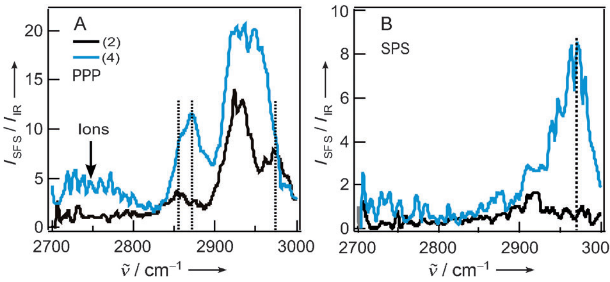

Figure 2. A comparison of vibrational sum frequency spectra of the $C_{16}H_{34}/D_2O$ droplet interface at pH 12 (sample (2), black lines), with the $C_{16}H_{34}/D_2O$ droplet interface prepared at neutral pH with 5 mm hexadecanoic acid (sample (4), blue lines). Shown are the PPP (A) and SPS polarization combinations (B). SSP data provided no new information.

also present at much lower concentrations and appear due to the interference of SF photons generated by hydrogenated oil molecules and SF photons generated by hydrogenated carboxylic acid chains. Likewise, the increase in the dispersive tail of the O–D vibrational modes is present. The spectrum of the uncontaminated sample (2) contains neither.

Since these spectra clearly show an absence of any features of carboxylic acids we conclude that at least for our experiments the charging of the oil/water interface is not due to impurities (for charge densities exceeding 0.036 $e^{-}nm^{-2}$, our current detection limit) but a property of the pristine oil/water interface. Assuming an area of 0.5–1 nm^2 per impurity it would leave at least 98.1–96.3 % of the oil/water surface clean, and 1.9–3.7 % of the surface with unknown purity. Such a surface coverage leaves interactions between water molecules and water and oil molecules as dominant driving forces for surface (and droplet) stability. We therefore propose that although surface impurities can never be ruled out entirely they are not the major source for the mobility of oil droplets in water. Indeed, gas bubbles display similar mobilities. Most commonly, the charge on the oil droplet (or gas bubble)/water interface is attributed to OH^- ions.[6a] Another explanation has been recently put forward,[2] based on charge transfer effects[6b] that occur between water molecules in a network. In a symmetric environment there is no net charge distribution. The interface, however, breaks the symmetry so that a net charge oscillation around the interface will appear. This explanation would favor the initial experimental SF data,[2,7] although more measurements are needed to make more definite conclusions as to what is the origin of the measured charge.

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